(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 141 377**
A2

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: 84112827.5

(22) Date of filing: 24.10.84

(51) Int. Cl.⁴: C 09 B 44/02
C 09 B 45/14, G 03 G 9/08

(30) Priority: 04.11.83 JP 205879/83
04.11.83 JP 205880/83
08.11.83 JP 208256/83
08.11.83 JP 208257/83

(43) Date of publication of application:
15.05.85 Bulletin 85/20

(84) Designated Contracting States:
BE DE FR GB

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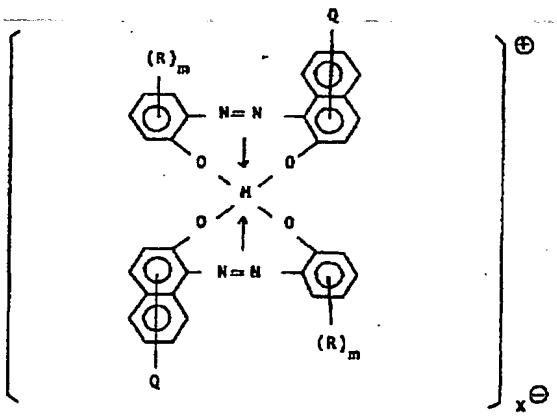
(54) **Metal complexes.**

(57) A symmetric 2 : 1 metal complex represented by the general formula:



where R is a hydrogen atom, an alkyl group having from 1 to 10 carbon atoms, an alkoxy group having from 1 to 4 carbon atoms, an alkoxycarbonyl group having from 2 to 5 carbon atoms, an acyl group having from 2 to 5 carbon atoms, an aminocarbonyl group, an alkylaminocarbonyl group having from 2 to 5 carbon atoms, an alkylsulfonyl group having from 1 to 3 carbon atoms, an aminosulfonyl group, an acylamino group having from 2 to 5 carbon atoms, a nitro group, a cyano group or a halogen atom, m is an integer of from 1 to 4, when m is 2 or more, the plurality of R may be the same or different substituents, Q is -NHCO-Y-Z or -CONH-Y-Z (where Y is an alkylene group having from 1 to 4 carbon atoms, and Z is a quaternary ammonium group), M is a chromium atom or a cobalt atom, and $X^{\ominus}$ is an anion.

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METAL COMPLEXES

The present invention relates to a metal complex and an electrophotographic toner containing the metal complex.

In electrophotography, it is common to employ a method which comprises forming an electrostatic latent image on a photoconductor made of e.g. a photoconductive material, then developing the latent image with a powder developer to form a visible image, and further fixing the image by heat or a solvent.

As the developer for such electrophotography, it is common to use a mixture comprising fine powder composed of a resin and a coloring agent, which is generally called a toner, and fine glass beads or iron powder, which is generally called a carrier.

The present invention relates to this developing powder called a toner and a novel metal complex useful for the toner.

A photoconductive layer can be positively or negatively charged, and a positively or negatively

charged electrostatic latent image can be formed in the photoconductive layer by exposing it with an original overlaid thereon. When a negatively charged electrostatic latent image is developed with a positively charged toner, a positive-positive image corresponding to the original will be formed. However, when a positively charged electrostatic latent image is developed with a negatively charged toner, a negative image of the original, i.e. a positive-negative image, where the black and white tones are reversed, will be obtained. Thus, as electrophotographic toners, there are two types of toners, i.e. one being a positively charged toner and the other being a negatively charged toner.

The present invention relates to a positively chargeable toner.

In general, such a toner is fine powder obtained by mixing a coloring agent such as a dyestuff or a pigment, to a synthetic resin.

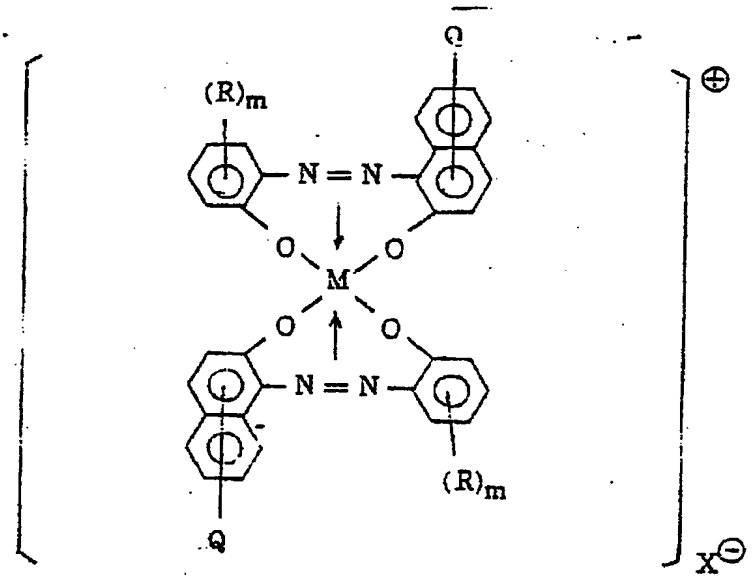
In order to positively charge the toner, the electrostatic characteristics of the dyestuff play an important role so that the dyestuff serves not only as a coloring agent but also as an electric charge-controlling agent.

As a positive charge-controlling agent, basic dyestuffs such as Nigrosine have been employed. However, the conventional dyestuffs such as Nigrosine have drawbacks such that there is a substantial variation in the electric chargeability among production lots, and

when formed into a toner the durability of the toner for continuous repeated use for photocopying is not good.

The present inventors have conducted extensive researches to solve the above problems, and have found certain metal complexes having a positive charge-controlling ability and good compatibility with resins. It is thereby possible to obtain excellent toners free from the above-mentioned problems.

Namely, the present invention provides a symmetric 2 : 1 metal complex represented by the general formula:



(I)

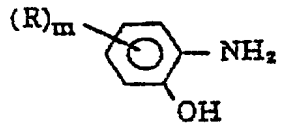
where R is a hydrogen atom, an alkyl group having from 1 to 10 carbon atoms, an alkoxy group having from 1 to 4 carbon atoms, an alkoxycarbonyl group having from 2 to 5 carbon atoms, an acyl group having from 2 to 5 carbon atoms, an aminocarbonyl group, an alkylaminocarbonyl

group having from 2 to 5 carbon atoms, an alkylsulfonyl group having from 1 to 3 carbon atoms, an aminosulfonyl group, an acylamino group having from 2 to 5 carbon atoms, a nitro group, a cyano group or a halogen atom, m is an integer of from 1 to 4, when m is 2 or more, the plurality of R may be the same or different substituents, Q is -NHCO-Y-Z or -CONH-Y-Z (where Y is an alkylene group having from 1 to 4 carbon atoms, and Z is a quaternary ammonium group), M is a chromium atom or a cobalt atom, and $X^{\ominus}$ is an anion.

The present invention also provides an electrophotographic toner containing the metal complex of the formula I as an electric charge-controlling agent or a coloring agent.

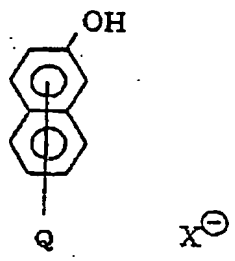
Now, the present invention will be described in detail with reference to the preferred embodiments.

The metal complex of the formula I of the present invention may be prepared in good yield by diazotizing a diazo component represented by the general formula:



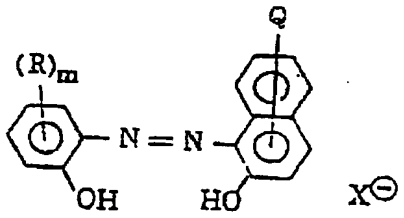
(II)

where R and m are as defined above, by a conventional method, then coupling the resulting diazo compound with a coupling component represented by the general formula:



(III)

where $X^{\ominus}$ and Q are as defined above, by a conventional method, to obtain a monoazo compound represented by the general formula:



(IV)

where R, m, $X^{\ominus}$ and Q are as defined above, and then heat-treating this monoazo compound with a chromium-introducing agent or a cobalt-introducing agent in water or in an organic solvent by a conventional method. As the diazo component of the formula II which may be used in the present invention, there may be mentioned, for instance, 3-chloro-2-aminophenol, 4-chloro-2-aminophenol, 4-bromo-2-aminophenol, 5-bromo-2-aminophenol, 4-iodo-2-aminophenol, 3,5-dichloro-2-aminophenol, 4,6-dichloro-2-aminophenol, 3,4,6-trichloro-2-aminophenol, 4-nitro-2-aminophenol, 5-nitro-2-aminophenol, 6-chloro-4-nitro-2-aminophenol, 4-chloro-5-nitro-2-aminophenol, 4-chloro-6-nitro-2-aminophenol, 6-bromo-4-nitro-2-aminophenol, 4-methyl-2-aminophenol, 4-t-butyl-2-aminophenol, 4-t-octyl-2-aminophenol, 4,5-dimethyl-2-aminophenol,

4-methoxy-2-aminophenol, 4-methyl-5-nitro-2-aminophenol, 4-bromo-5-methyl-2-aminophenol, 4-cyano-2-aminophenol, 4-acetyl-2-aminophenol, 4-methoxycarbonyl-2-aminophenol, 4-aminocarbonyl-2-aminophenol, 4-ethylaminocarbonyl-2-aminophenol, 4-aminosulfonyl-2-aminophenol and 4-propylsulfonyl-2-aminophenol.

As the coupling component of the formula III where Q is -NHCO-Y-Z, there may be mentioned N,N,N-trimethyl-N-[N'-(7-hydroxy-1-naphthyl)carbamoyl]methylammonium chloride, N,N,N-trimethyl-N-[N'-(6-hydroxy-1-naphthyl)-carbamoyl]methylammonium chloride, N,N,N-triethyl-N-[N'-(7-hydroxy-1-naphthyl)carbamoyl]methylammonium chloride, N,N-dimethyl-N-ethyl-N-[N'-(7-hydroxy-1-naphthyl)-carbamoyl]methylammonium iodide, N,N-dimethyl-N-n-butyl-N-[N'-(7-hydroxy-1-naphthyl)carbamoyl]methylammonium bromide, N,N-dimethyl-N-n-butyl-N-[N'-(6-hydroxy-1-naphthyl)carbamoyl]methylammonium chloride, N,N,N-trimethyl-N-[N'-(7-hydroxy-1-naphthyl)carbamoyl]propyl-ammonium chloride, N,N,N-trimethyl-N-[N'-(6-hydroxy-1-naphthyl)carbamoyl]propylammonium chloride, N,N-dimethyl-N-benzyl-N-[N'-(7-hydroxy-1-naphthyl)carbamoyl]methyl-ammonium chloride, N-methyl-N-[N'-(7-hydroxy-1-naphthyl)-carbamoyl]propylpiperidinium bromide, N-methyl-N-[N'-(7-hydroxy-1-naphthyl)carbamoyl]methylmorpholinium chloride, N-[N'-(7-hydroxy-1-naphthyl)carbamoyl]methylpyridinium chloride, and N-[N'-(6-hydroxy-1-naphthyl)carbamoyl]-methylpyridinium chloride.

Further, as the coupling component of the formula III where Q is -CONH-Y-Z, there may be mentioned N,N,N-trimethyl-N-2-(3-hydroxy-2-naphthamido)ethylammonium chloride, N,N,N-triethyl-N-2-(3-hydroxy-2-naphthamido)-ethylammonium chloride, N,N,N-trimethyl-N-3-(3-hydroxy-2-naphthamido)propylammonium bromide, N,N-dimethyl-N-ethyl-N-3-(3-hydroxy-2-naphthamido)propylammonium chloride, N,N,N-trimethyl-N-4-(3-hydroxy-2-naphthamido)-butylammonium chloride, N,N-dibutyl-N-methyl-N-3-(3-hydroxy-2-naphthamido)propylammonium chloride, N-methyl-N-3-(3-hydroxy-2-naphthamido)propylpiperidinium bromide, N-methyl-N-3-(3-hydroxy-2-naphthamido)propylmorpholinium chloride and N-2-(3-hydroxy-2-naphthamido)ethylpyridinium chloride.

The metal complex of the formula I of the present invention thus obtained, has a positive chargeability and excellent compatibility with resins, for example, a polymer of styrene or a substituted styrene such as polystyrene or polyvinyl toluene, a styrene-substituted styrene copolymer, a styrene-acrylate copolymer, a styrene-methacrylate copolymer, a styrene-acrylonitrile copolymer, a polyvinyl chloride resin, a polyethylene, a silicone resin, a polyester, a polyurethane, a polyamide, an epoxy resin, a modified rosin or a phenol resin. Thus, the metal complex can uniformly be dispersed in such a resin and further pulverized into fine powder. Such a fine powder also has positive chargeability.

On the other hand, the metal complex of the present invention has little solubility in water, and scarcely affected by the environmental humidity, thus being capable of maintaining the positive chargeability for a long period of time.

In the formula I, $X^{\ominus}$ is preferably a halogen ion such as a chlorine, bromine, fluorine or iodine ion.

The toner of the present invention may be prepared by melt-mixing from 1 to 50% by weight of the metal complex of the formula I with 50 to 99% by weight of a synthetic resin, and after the solidification, pulverizing the solidified product by means of a ball mill or other pulverizer. Alternatively, it may be prepared by adding a polymerization initiator to a synthetic resin monomer, incorporating from 1 to 50%, by weight of the monomer, of the metal complex of the formula I thereto, and polymerizing the mixture in a suspended state in water. Other coloring agents or carbon black may also be incorporated. The toner thus obtained will provide an electric charge in a quantity suitable for the development of an electrostatic image due to the friction with the carrier, whereby the quantity of the electric charge can be maintained at a constant level during repeated development operations. The distribution of the electric charge is uniform and can be maintained in a stabilized condition for a long period of time.

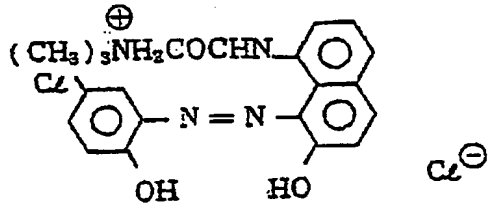
Accordingly, an image developed by means of this toner, is uniform and has a constant image density, and it is very sharp as compared with the image where a conventional positive toner is used.

Now, the present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is by no means restricted by these specific Examples.

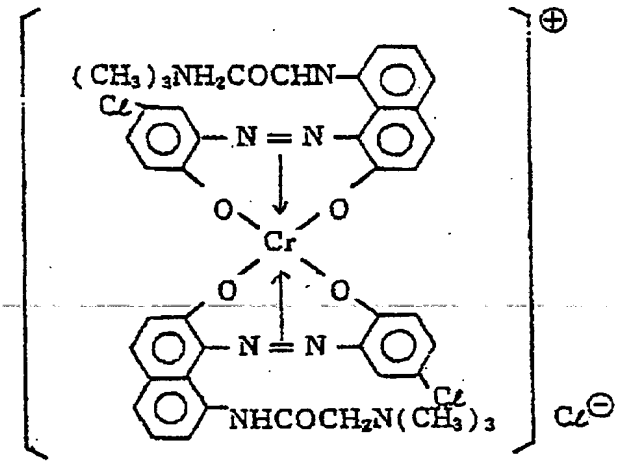
In the Examples, "parts" means "parts by weight".

EXAMPLE 1:

14.4 Parts of 4-chloro-2-aminophenol was mixed with 26 parts of concentrated hydrochloric acid and 400 parts of water, and the mixture was cooled with ice to a temperature of from 0 to 5°C. After an addition of 6.9 parts of sodium nitrite, the mixture was stirred at the same temperature for 2 hours for diazotization. The diazo compound thus obtained was subjected to a coupling reaction by pouring it into a solution of a mixture comprising 300 parts of water, 10 parts of sodium hydroxide and 29.3 parts of N,N,N-trimethyl-N-[N'-(7-hydroxy-1-naphthyl)carbamoyl] methylammonium chloride at a temperature of from 0 to 5°C. Then, a monoazo compound having the following structure was isolated.



This monoazo compound was dissolved in 120 parts of ethylene glycol, and 17.4 parts of sodium chromium salicylate was added thereto. The mixture was stirred at a temperature of from 85 to 90°C for a chromium-introducing reaction. Then, the mixture was cooled to 30°C, and hydrochloric acid was added to acidify the mixture to an acidity confirmed by Congo Red. Then, the product was isolated at room temperature, and dried under reduced pressure at 50 to 60°C to obtain 45 parts of chromium complex of the following formula as a blackish blue fine powder:

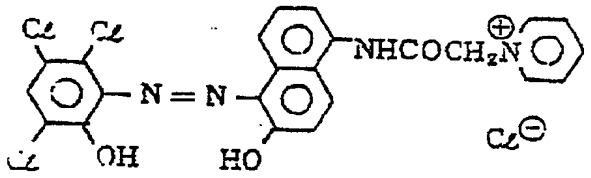


The wavelength at the maximum absorption by this chromium complex was 581 nm as measured in a dimethylformamide solvent.

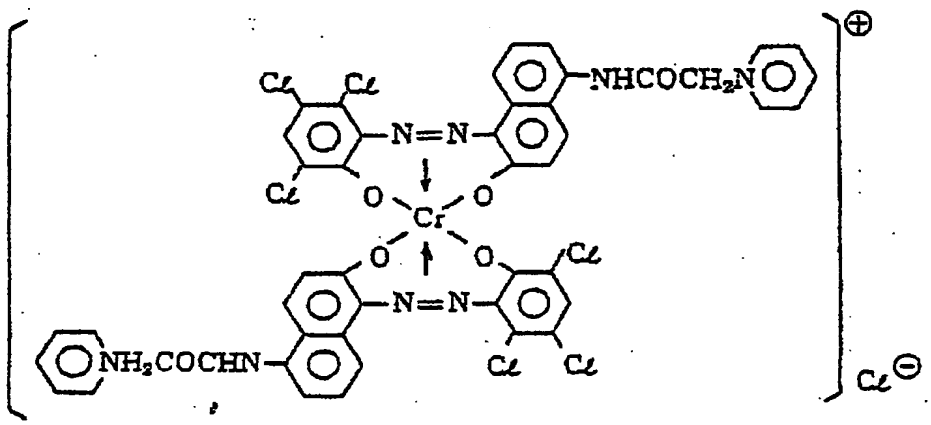
The coupling component used in this Example was prepared by chloroacetylating 8-amino-2-naphthol in glacial acetic acid with chloroacetic acid chloride by using sodium acetate as an acid binding agent, to obtain 8-chloroacetylamino-2-naphthol, dissolving isolated 8-chloroacetylamino-2-naphthol in acetone, and then blowing gaseous trimethylamine into the solution.

EXAMPLE 2:

53.8 Parts of a monoazo dyestuff represented by the formula:



obtained in the same manner as in Example 1, was dissolved in 200 parts of methyl cellosolve, and after an addition of 18.2 parts of sodium chromium salicylate, the mixture was stirred at a temperature of from 100 to 105°C for 2 hours for a chromium-introducing reaction. Then, the mixture was cooled to 20°C, and then treated in the same manner as in Example 1 to obtain 51.2 parts of a chromium complex of the following formula as a black powder:

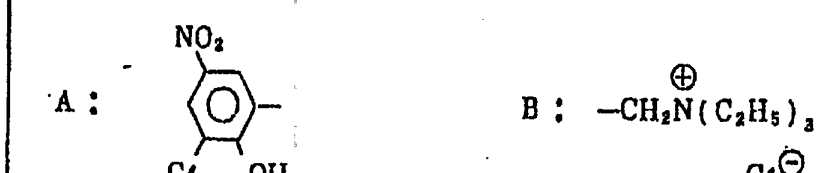
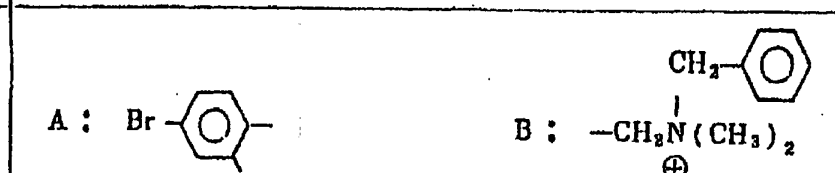


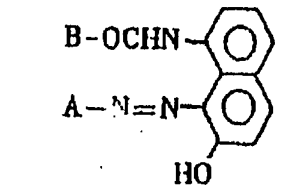
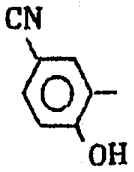
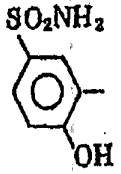
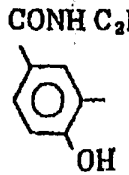
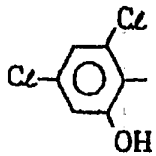
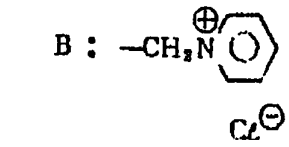
The wavelength at the maximum absorption by this chromium complex was 594 nm as measured in a dimethylformamide solvent.

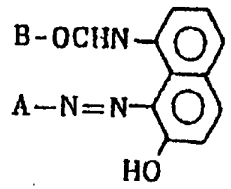
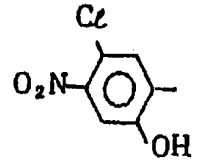
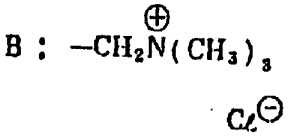
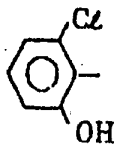
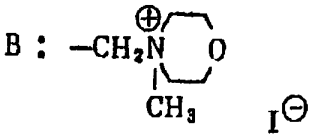
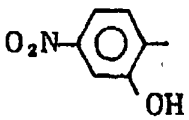
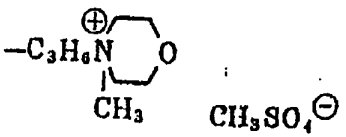
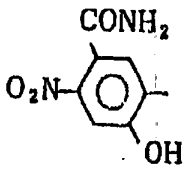
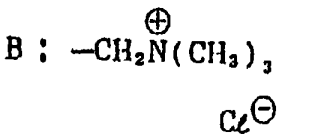
The coupling component used in this Example was readily prepared by heating 5-chloroacetylamino-2-napnthol in pyridine.

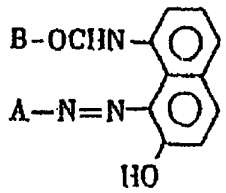
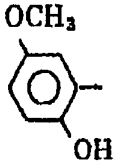
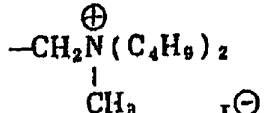
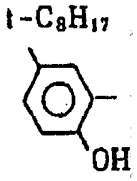
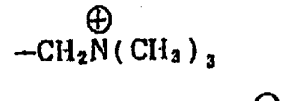
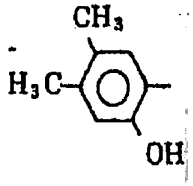
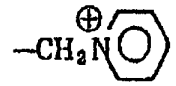
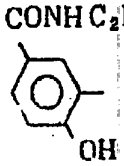
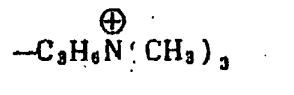
EXAMPLES 3 to 32:

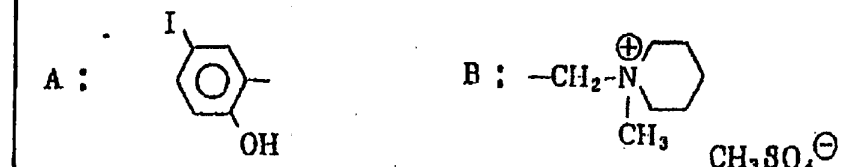
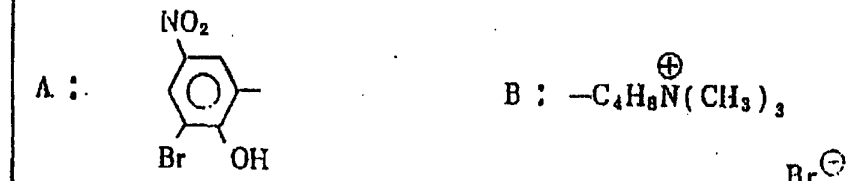
In the same manner as in Examples 1 and 2, symmetric 2 : 1 metal complexes were obtained. The structures, the wavelengths at the maximum absorption (in dimethylformamide) and outer appearance are shown in Table 1.

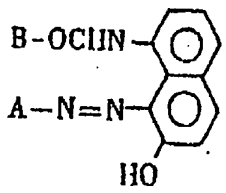
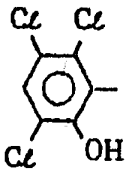
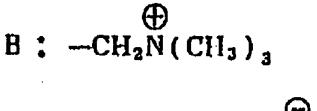
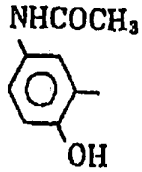
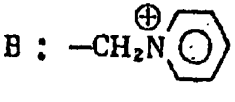
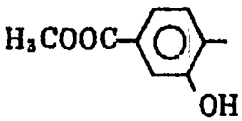
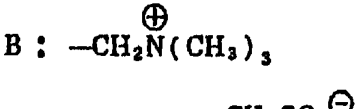
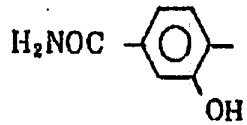
Examples	Monoazo compound	Central metal	Complexing solvent	Wavelength at the maximum absorption (nm)	Outer appearance
3		Cr	Ethylene glycol	576	Black powder
4		Cr	Dimethyl-formamide	583	Blackish purple powder
5		Cr	Ethylene glycol	592	Black powder
6		Cr	Water	597	Blackish purple powder

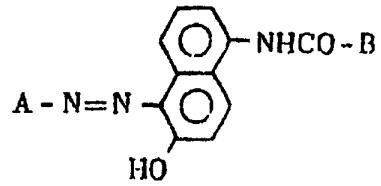
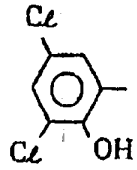
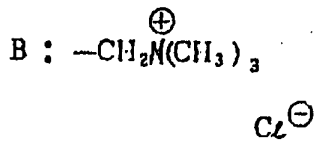
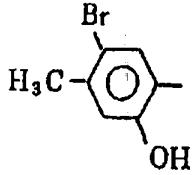
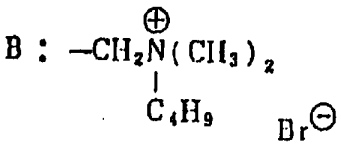
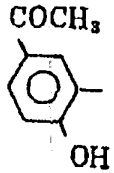
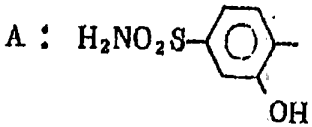
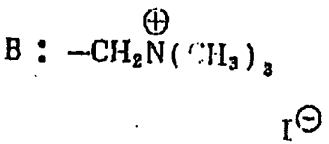
Examples	Monoazo compound		Central metal	Complexing solvent	Wavelength at the maximum absorption (nm)	Outer appearance
						
7	A : 	B : $-C_2H_4\overset{\oplus}{N}(CH_3)_3$ $C\ell^{\ominus}$	Co	Water	562	Black powder
8	A : 	B : $-CH_2\overset{\oplus}{N}(CH_3)_2$ C_2H_5 $C\ell^{\ominus}$	Cr	Methyl cellosolve	585	Black powder
9	A : 	B : $-CH_2\overset{\oplus}{N}(CH_3)_3$ $C\ell^{\ominus}$	Co	n-Butanol	560	Black powder
10	A : 	B : 	Cr	Dimethyl sulfoxide	592	Black powder

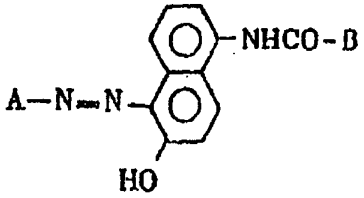
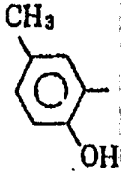
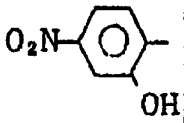
Examples	Monoazo compound 	Central metal	Complexing solvent	Wavelength at the maximum absorption (nm)	Outer appearance
11	A :  B : 	Cr	Formamide Water	612	Black powder
12	A :  B : 	Cr	Ethylene glycol	587	Blackish purple powder
13	A :  B : 	Cr	Ethylene glycol	613	Black powder
14	A :  B : 	Cr	Water Dimethyl-formamide	608	Black powder

Examples	Monoazo compound 	Central metal	Complexing solvent	Wavelength at the maximum absorption (nm)	Outer appearance
15	A :  B : 	Cr	Ethylene glycol	589	Black powder
16	A :  B : 	Cr	Ethylene glycol	590	Blackish purple powder
17	A :  B : 	Cr	Water	593	Blackish blue powder
18	A :  B : 	Co	Ethylene glycol	559	Blackish purple powder

Examples	Monoazo compound	Central metal	Complexing solvent	Wavelength at the maximum absorption (nm)	Outer appearance
19		Cr	Methyl cellosolve	592	Black powder
20		Cr	Diethylene glycol	588	Blackish blue powder
21		Cr	Ethylene glycol	596	Blackish purple powder
22		Cr	Methyl cellosolve	592	Black powder

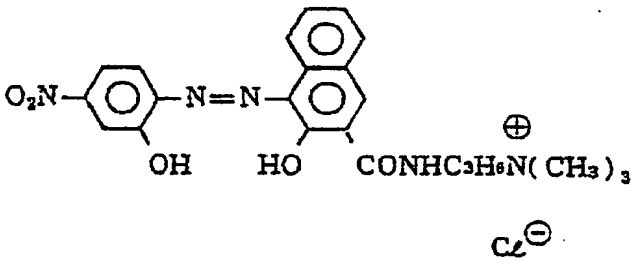
Examples	Monoazo compound 	Central metal	Complexing solvent	Wavelength at the maximum absorption (nm)	Outer appearance
23	A :  B : 	Cr	Triethanolamine	582	Black powder
24	A :  B : 	Cr	n-Butanol	587	Blackish blue powder
25	A :  B : 	Cr	Ethylene glycol	594	Black powder
26	A :  B : 	Cr	Ethylene glycol	593	Black powder

Examples	Monoazo compound 	Central metal	Complexing solvent	Wavelength at the maximum absorption (nm)	Outer appearance
27	A :  B : 	Cr	n-Butanol	592	Black powder
28	A :  B : 	Cr	Ethylene glycol	586	Blackish purple powder
29	A :  B : 	Cr	Methyl cellosolve	590	Blackish blue powder
30	A :  B : 	Cr	Methyl cellosolve	593	Black powder

Examples	Monoazo compound 	Central metal	Complexing solvent	Wavelength at the maximum absorption (nm)	Outer appearance
31	A :  B : $-C_3H_6\overset{\oplus}{N}(CH_3)_3$ $Cl^{\ominus}$	Cr	Ethylene glycol	585	Black powder
32	A :  B : $-CH_2\overset{\oplus}{N}(C_2H_5)_3$ $Br^{\ominus}$	Cr	Dimethylformamide	616	Black powder

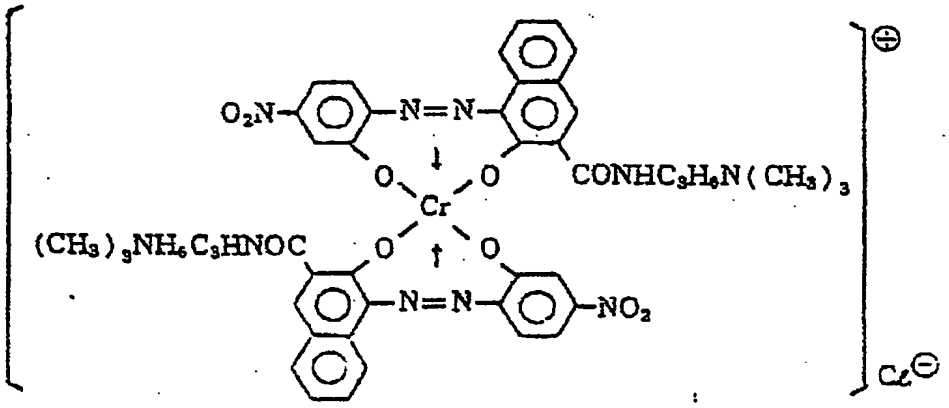
EXAMPLE 33:

15.4 Parts of 5-nitro-2-aminophenol was mixed with 26 parts of concentrated hydrochloric acid and 250 parts of water, and the mixture was cooled with ice to a temperature of from 0 to 5°C. After an addition of 6.9 parts of sodium nitrite, the mixture was stirred at the same temperature for 1.5 hours for diazotization. The diazo compound thus obtained was subjected to a coupling reaction by pouring it into a solution comprising 400 parts of water, 10 parts of sodium hydroxide and 39.9 parts of N,N,N-trimethyl-N-3-(3-hydroxy-2-naphthamido)-propylammonium methylsulfate at a temperature of from 0 to 5°C. Then, a monoazo compound represented by the formula:



was isolated. This monoazo compound was dissolved in 150 parts of methyl cellosolve, and 17.5 parts of sodium chromium salicylate was added thereto. The mixture was stirred at from 90 to 95°C for 2 hours for a chromium-introducing reaction. Then, the reaction mixture was cooled to 25°C, and hydrochloric acid was added to acidify the mixture. Then, the product was isolated and dried under reduced pressure at a temperature of from 50

to 60°C to obtain 56 parts of a chromium complex having the following formula as a blackish purple powder:

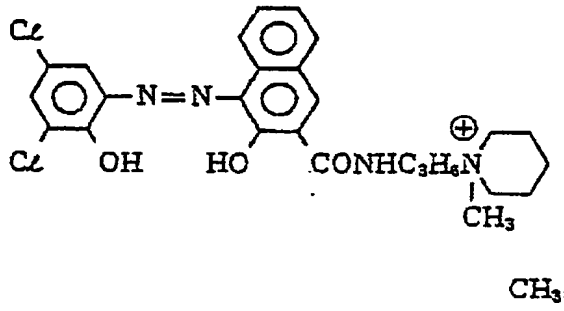


The visible ray absorption spectrum of this chromium complex was measured in a dimethylformamide solvent, whereby the wavelength at the maximum absorption was 599 nm.

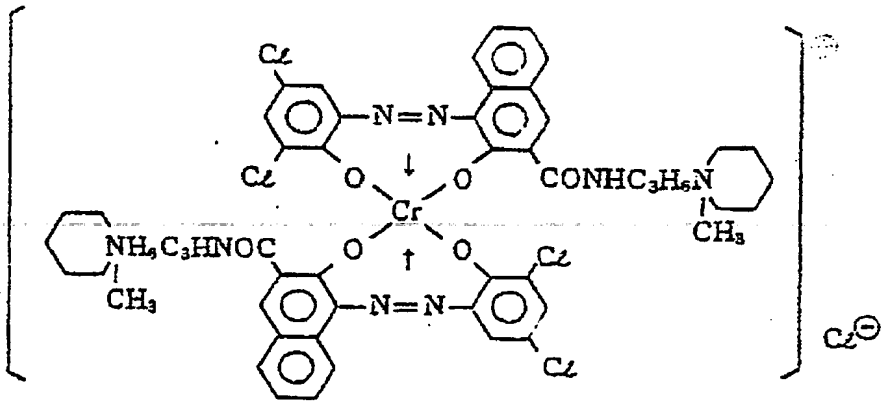
The coupling component used in this Example was obtained by reacting methyl 2-hydroxy-3-naphthoate with dimethylamino propylamine in toluene to obtain N,N-dimethyl-N-3-(3-hydroxy-2-naphthamido)propylamine, and converting the amide compound isolated by filtration, with dimethylsufuric acid in methanol, to a quaternary ammonium form. Further, the amide compound may also be readily prepared via 2-hydroxy-3-napthoic acid chloride.

EXAMPLE 34:

62.8 Parts of a monoazo dyestuff of the formual:



obtained in the same manner as in Example 33, was dissolved in 200 parts of dimethylformamide, and after an addition of 30.5 parts of chromium acetate (45% solution), the mixture was stirred at a temperature of from 100 to 105°C for 3 hours for a chromium-introducing reaction. Then, the mixture was treated in the same manner as in Example 33 to obtain 54.3 parts of a chromium complex of the following formula as a blackish purple fine powder:

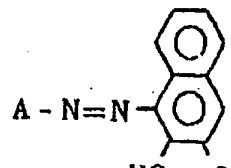
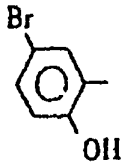
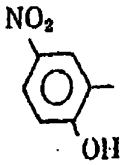
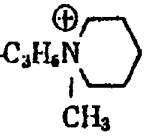
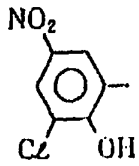
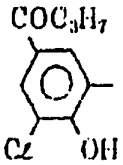


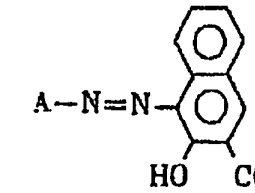
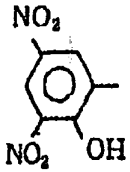
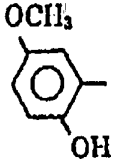
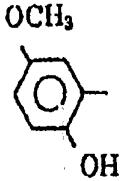
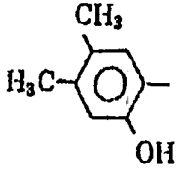
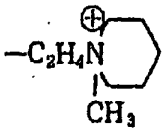
The visible ray absorption spectrum of this chromium complex was measured in a dimethylformamide solvent, whereby the wavelength at the maximum absorption was 602 nm.

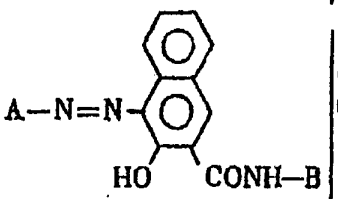
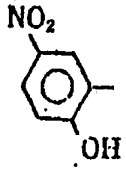
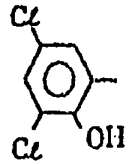
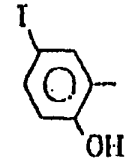
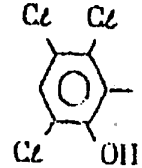
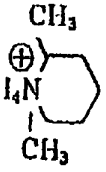
EXAMPLES 35 to 58:

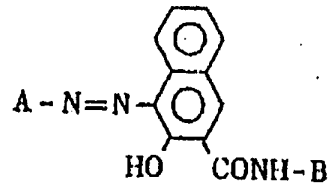
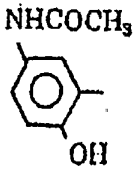
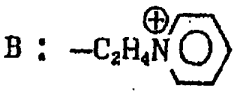
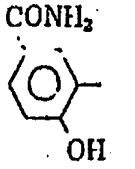
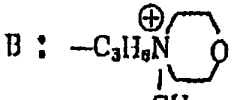
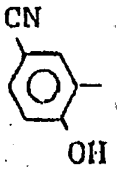
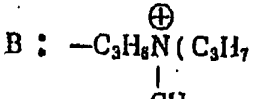
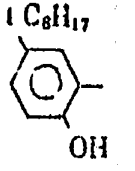
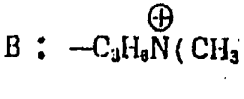
In the same manner as in Examples 33 and 34, metal complexes were prepared. The structures, the wavelengths at the maximum absorption and the outer appearances of these metal complexes are shown in Table 2.

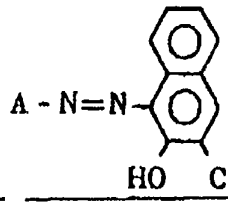
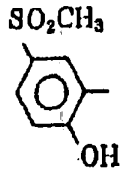
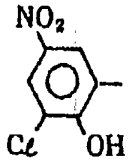
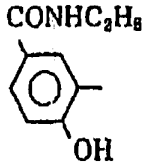
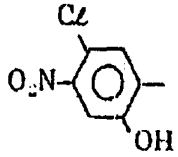
Table 2

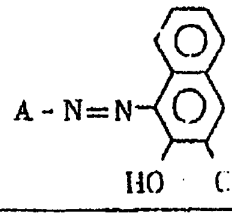
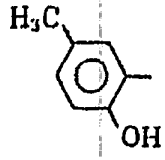
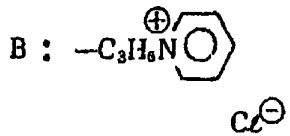
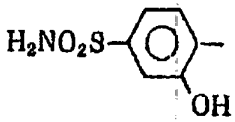
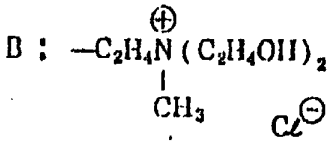
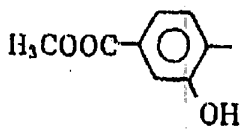
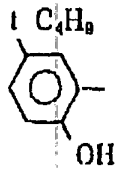
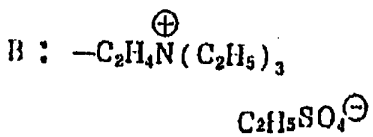
Examples	Monoazo compound 	Central metal	Complexing solvent	Wavelength at the maximum absorption (nm)	Outer appearance
35	A :  B : $-C_3H_6\overset{\oplus}{N}(CH_3)_3$ $Cl^{\ominus}$	Cr	Ethylene glycol	595	Black powder
36	A :  B :  $Cl^{\ominus}$	Cr	Ethylene glycol	591	Blackish blue powder
37	A :  B : $-C_2H_4\overset{\oplus}{N}(C_2H_5)_3$ $Cl^{\ominus}$	Cr	Dimethylformamide	601	Blackish purple powder
38	A :  B :  $Br^{\ominus}$	Cr	Ethylene glycol	587	Black powder

Examples	Monoazo compound		Central metal	Complexing solvent	Wavelength at the maximum absorption (nm)	Outer appearance
						
39	A : 	B : $-C_4H_8\overset{\oplus}{N}(CH_3)_3$ $C\ell^{\ominus}$	Cr	Water Ethylene glycol	598	Blackish blue powder
40	A : 	B : $-C_2H_4\overset{\oplus}{N}(CH_3)_3$ $C\ell^{\ominus}$	Co	Ethylene glycol	572	Blackish blue powder
41	A : 	B : $-C_2H_4\overset{\oplus}{N}(C_2H_5)_2$ CH_3 $C\ell^{\ominus}$	Cr	n-Butanol	587	Black powder
42	A : 	B :  $I^{\ominus}$	Cr	Ethylene glycol	586	Black powder

Examples	Monoazo compound 	Central metal	Complexing solvent	Wavelength at the maximum absorption (nm)	Outer appearance
43	A :  B : $-C_3H_6\overset{\oplus}{N}(CH_3)_3$ $CH_3SO_4^{\ominus}$	Cr	Ethylene glycol	593	Blackish blue powder
44	A :  B : $-C_3H_6\overset{\oplus}{N}(C_4H_9)_2$ CH_3 $Cl^{\ominus}$	Co	Methyl cellosolve	571	Blackish purple powder
45	A :  B : $-C_3H_6N(CH_3)_2$ C_2H_5 $Cl^{\ominus}$	Cr	n-Butanol	590	Black powder
46	A :  B :  CH_3 $Cl^{\ominus}$	Cr	Ethylene glycol	610	Black powder

Examples	Monoazo compound 	Central metal	Complexing solvent	Wavelength at the maximum absorption (nm)	Outer appearance
47	A :  B : 	Cr	Ethylene glycol	587	Black powder
48	A :  B : 	Cr	Ethylene glycol	592	Blackish blue powder
49	A :  B : 	Cr	Dimethylformamide	595	Blackish blue powder
50	A :  B : 	Co	Triethanolamine	568	Blackish purple powder

Examples	Monoazo compound		Central metal	Complexing solvent	Wavelength at the maximum absorption (nm)	Outer appearance
51	A : 	B : $-C_3H_6\overset{\oplus}{N}(CH_3)_3$ $Cl^{\ominus}$	Cr	Water	590	Black powder
52	A : 	B : $-C_2H_4\overset{\oplus}{N}(CH_3)_2$ $C_{18}H_{37}$ $Cl^{\ominus}$	Cr	Ethylene glycol	598	Black powder
53	A : 	B : $-C_3H_6\overset{\oplus}{N}(CH_3)$ C_2H_4OH $Cl^{\ominus}$	Cr	Diethylene glycol	586	Blackish purple powder
54	A : 	B : $-C_2H_4\overset{\oplus}{N}(CH_3)_3$ $Br^{\ominus}$	Cr	Ethylene glycol	593	Black powder

Examples	Monoazo compound 	Central metal	Complexing solvent	Wavelength at the maximum absorption (nm)	Outer appearance
55	A :  B : 	Cr	Dimethylformamide	588	Black powder
56	A :  B : 	Cr	Water	592	Black powder
57	A :  B : 	Cr	Dimethylformamide	600	Black powder
58	A :  B : 	Cr	Ethylene glycol	594	Blackish blue powder

Now, the following Application Examples are given to illustrate the toners of the present invention.

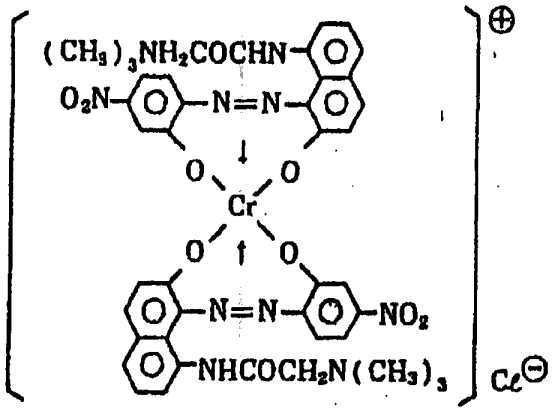
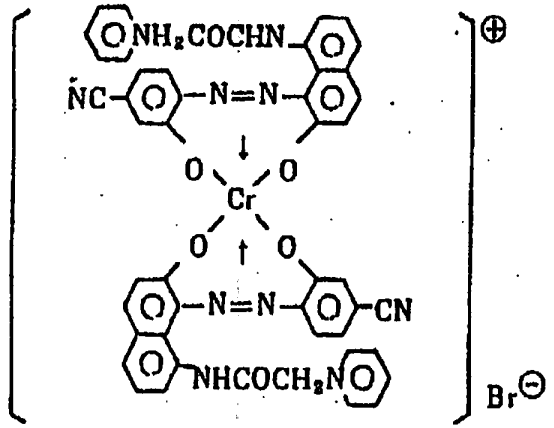
Application Example 1:

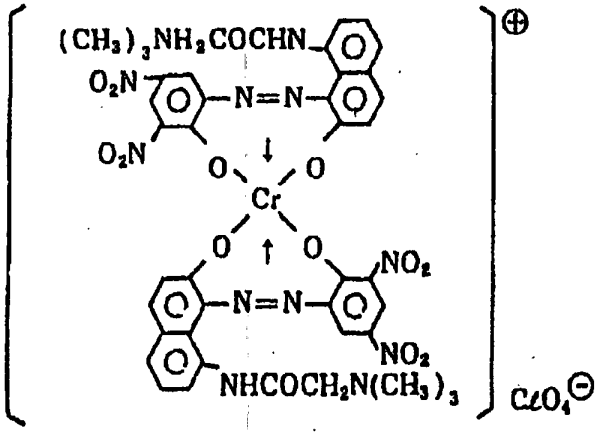
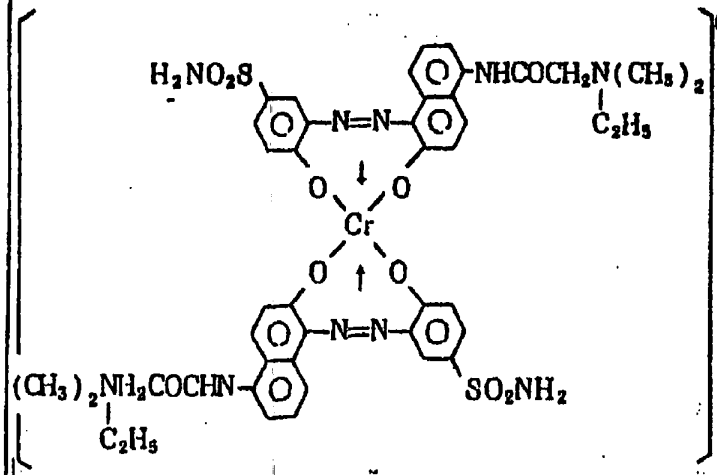
To 5 parts of the chromium complex obtained in Example 1, 100 parts of a styrene-n-butyl methacrylate copolymer and 5 parts of carbon black were added and thoroughly mixed. Then, the mixture was kneaded while heating and melting it. After cooling, the mixture was roughly pulverized in a mixer, and then finely pulverized by a high speed centrifugal pulverizer to obtain a positively chargeable fine toner. The toner was mixed with iron powder having a particle size of from 100 to 150 μm in a weight ratio of 5 : 100, and the mixture was used for a commercially available copying machine employing a zinc oxide photosensitive material, whereby a clear image free from fogging was obtained. The quantity of the electric charge of the toner was 22 μc/g on an average as measured by a blow off method, and the electric charge distribution was substantially uniform at a level of from 22 to 23 μc/g.

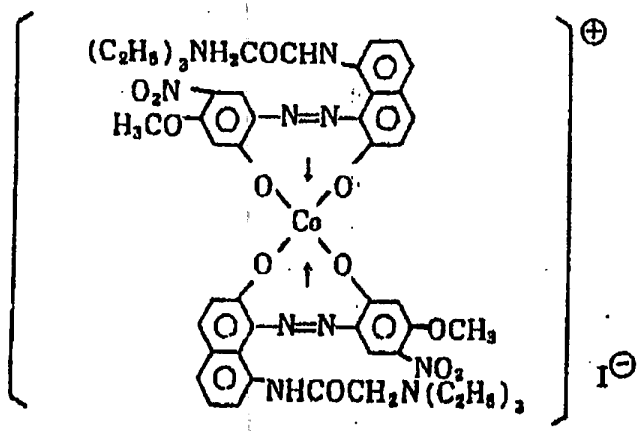
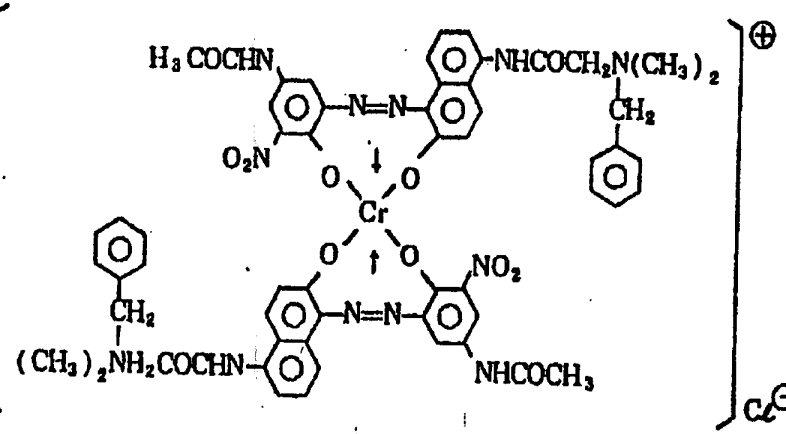
Application Examples 2 to 13:

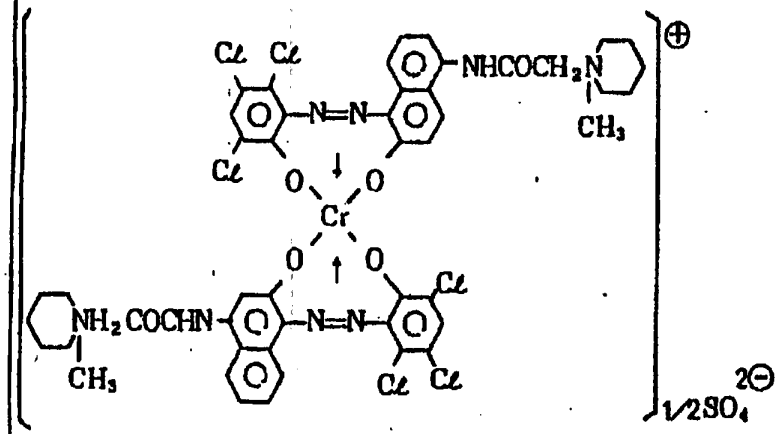
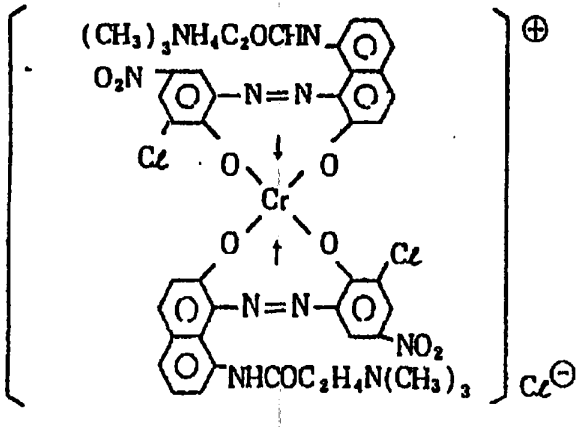
In the same manner as in Application Example 1, toners containing metal complexes and having compositions as identified in Table 3 were prepared. The electric chargeability of these toners was measured. The results are also shown in Table 3.

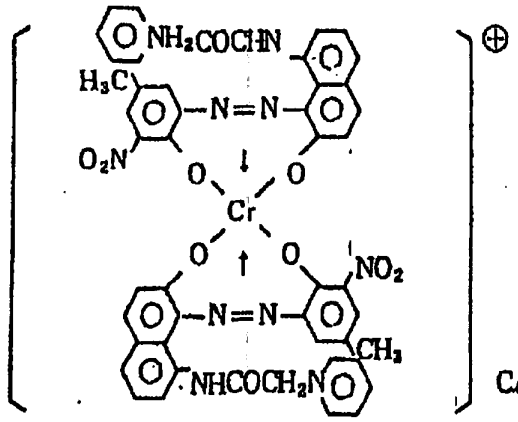
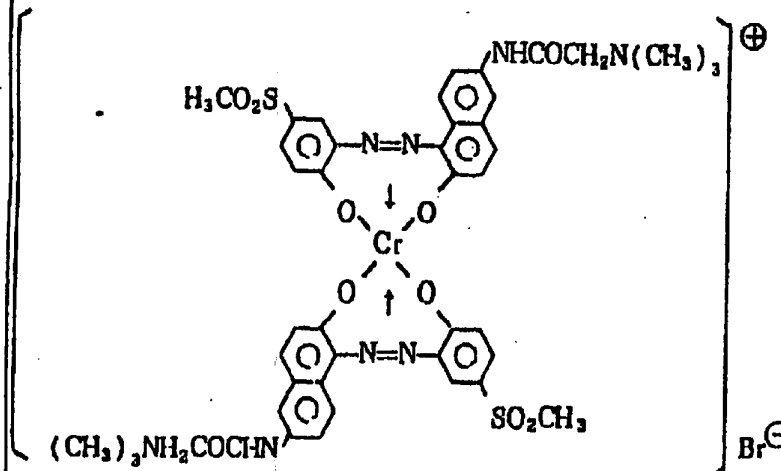
Table 3

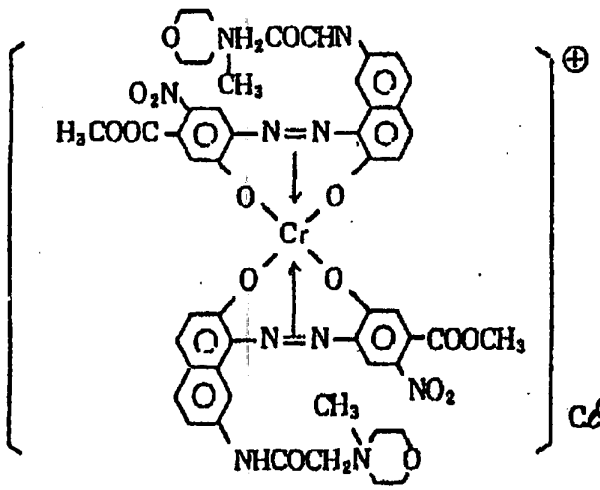
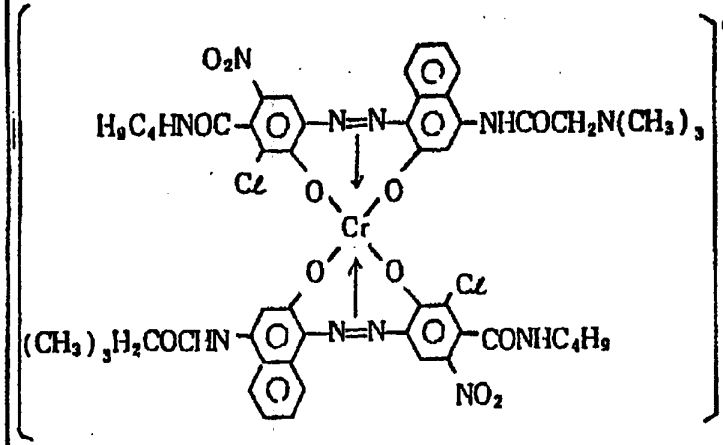
Application Examples	Composition of the developer			Electric chargeability (μc/g)
	Metal complex		Other components	
2		0.2 part	Styrene-n-butyl methacrylate copolymer 20 parts Carbon black 1 part Iron powder carrier 500 parts	18.3
3		0.5 part	Phenol resin 12 parts Polyester resin 9 parts Carbon black 1.5 parts Iron powder carrier 500 parts	16.8

Application Examples	Composition of the developer		Electric chargeability (μc/g)
	Metal complex	Other components	
4	 1 part	Polyethylene wax 50 parts Ethylene-vinyl acetate copolymer 40 parts Magnetite 50 parts	17.3
5	 0.1 part	Styrene-ethylhexyl methacrylate copolymer 40 parts Polyester resin 5 parts Silicone wax 4 parts Carbon black 0.1 part Silicone resin-coated iron powder carrier 700 parts	10.3

Application Examples	Composition of the developer		Electric chargeability (μc/g)
	Metal complex	Other components	
6	 0.2 part	Styrene-acryl copolymer 20 parts Carbon black 2 parts Glass beads carrier 1000 parts	15.4
7	 5 parts	Styrene-ethyl methacrylate copolymer 100 parts Iron powder carrier 2000 parts	13.2

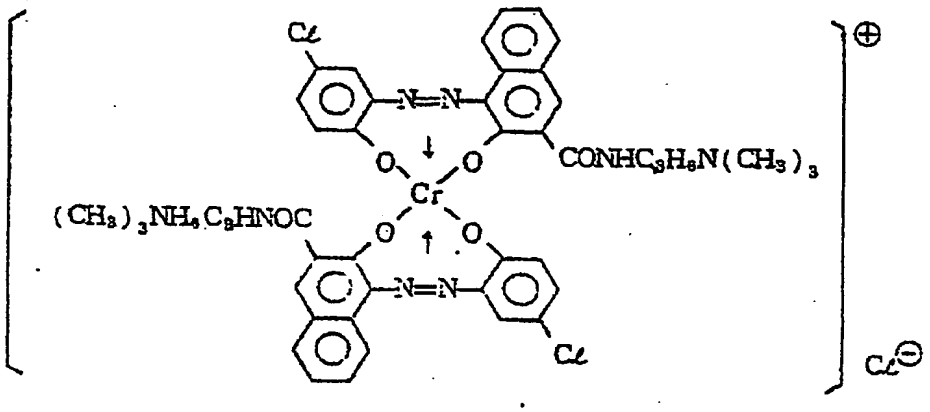
Application Examples	Composition of the developer		Electric chargeability (μc/g)
	Metal complex	Other components	
8	 2 parts	Styrene-butadiene copolymer 50 parts Carbon black 5 parts Iron powder carrier 1500 parts	18.9
9	 0.5 part	Styrene-n-butyl methacrylate copolymer 12 parts C.I. pigment blue-15 0.1 part Iron powder carrier 500 parts	17.4

Application Examples	Composition of the developer		Electric chargeability (μc/g)
	Metal complex	Other components	
10	 1 part	Polyester resin 50 parts Carbon black 5 parts Iron powder carrier 1500 parts	12.1
11	 1 part	Styrene-methyl acrylate copolymer 50 parts C.I. pigment black 1 3 parts Iron powder carrier 1500 parts	12.8

Application Examples	Composition of the developer		Electric chargeability (μc/g)
	Metal complex	Other components	
12	 0.5 part	Epoxy resin 30 parts Carbon black 3 parts Iron powder carrier 1000 parts	11.1
13	 0.5 part	Polyvinyl butyral resin 10 parts Carbon black 1 part Iron powder carrier 250 parts	14.2

Application Example 14:

To 1 part of a chromium complex represented by the formula:

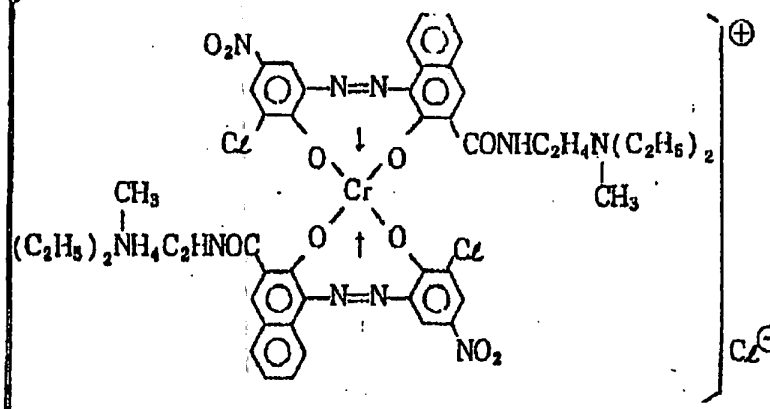
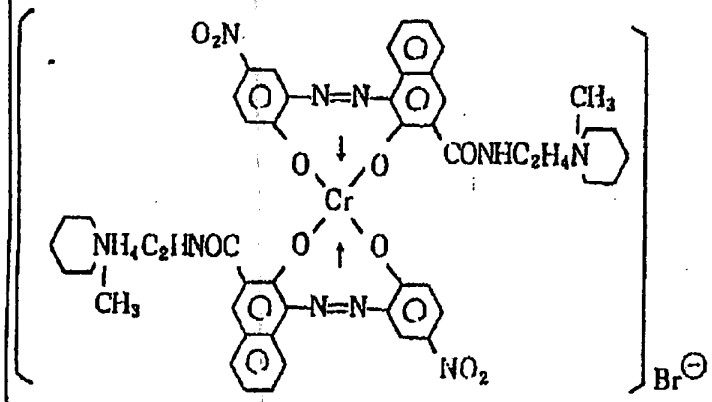


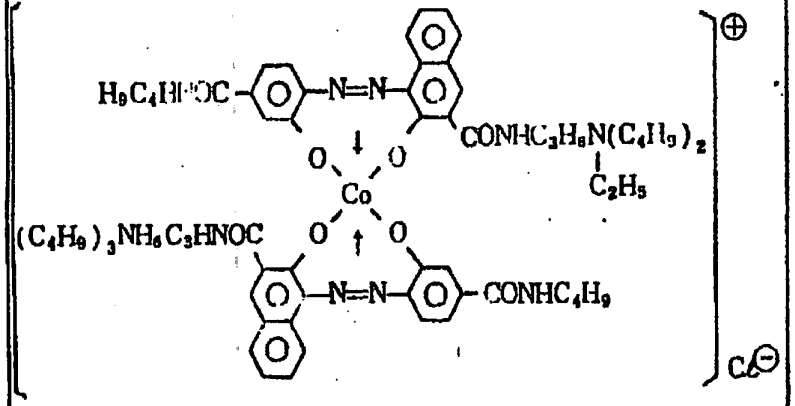
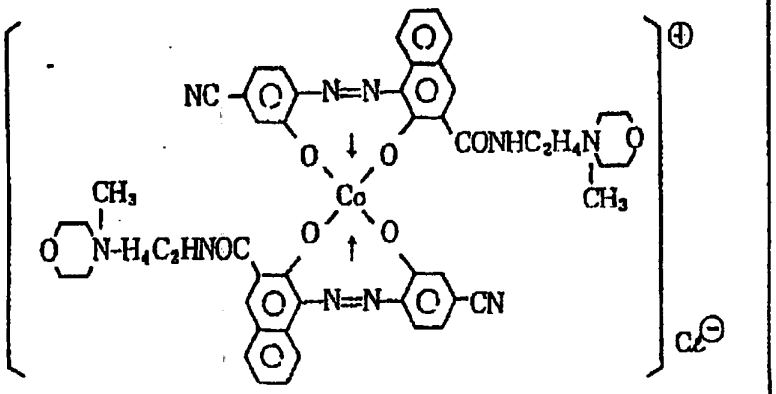
100 parts of a styrene-n-butyl methacrylate copolymer and 8 parts of carbon black were added and thoroughly mixed. The mixture was then kneaded while heating and melting it. After cooling, the mixture was roughly pulverized in a mixer, and then finely pulverized by a high speed centrifugal pulverizer to obtain a positively chargeable fine toner. The toner was mixed with iron powder having a particle size of from 100 to 150 μm in a weight ratio of 5 : 100, and the mixture was used for a commercially available copying machine employing a zinc oxide photosensitive material, whereby a clear image free from fogging was obtained. The quantity of the electric charge of the toner was 17.5 μc/g on an average as measured by a blow off method, and the electric charge distribution was substantially uniform at a level of from 17.0 to 18.3 μc/g.

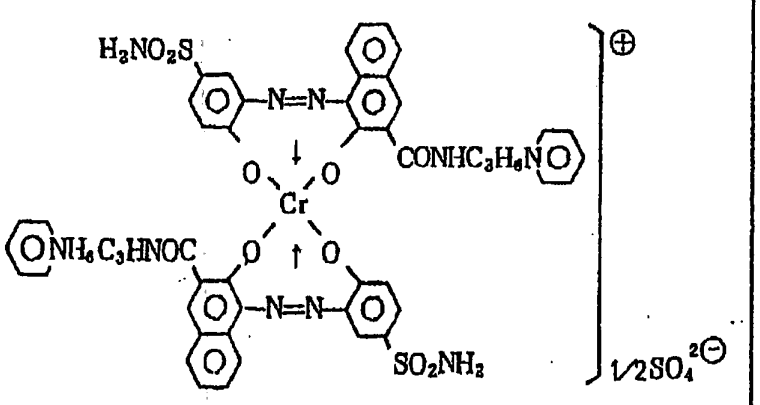
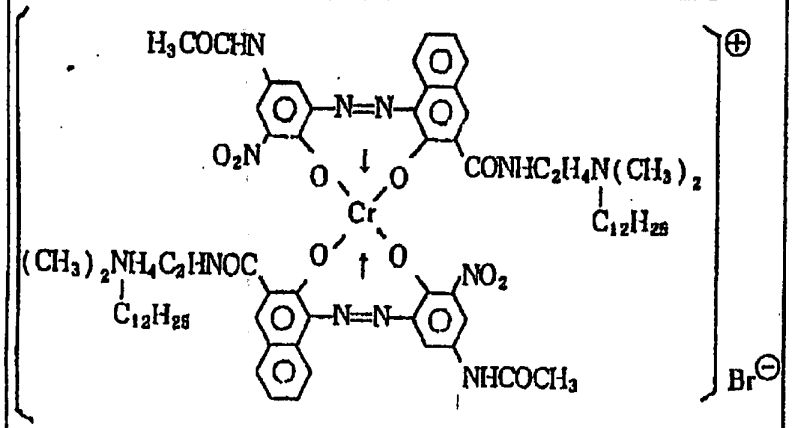
Application Examples 15 to 29:

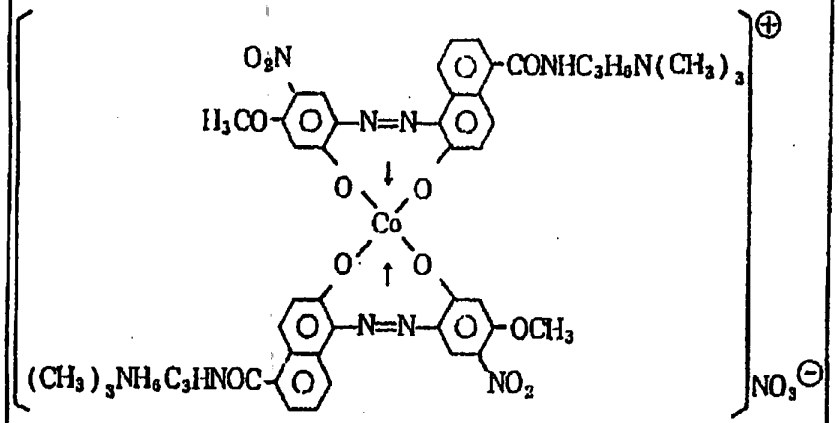
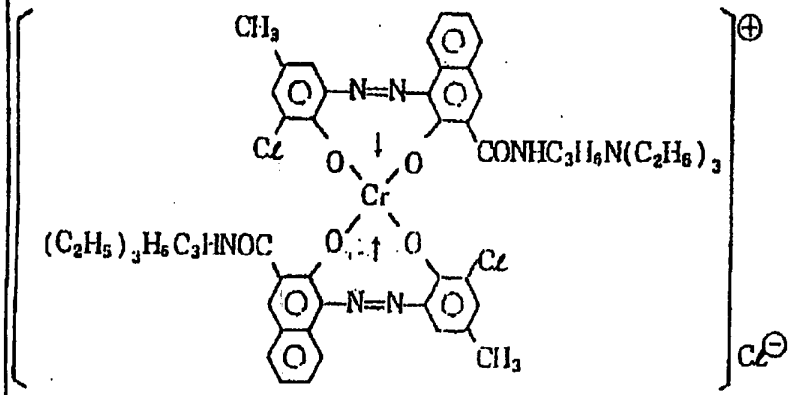
In the same manner as in Example 14, toners containing metal complexes and having compositions as identified in Table 4 were obtained. The electric chargeability of these toners were measured. The results are also shown in the Table 4.

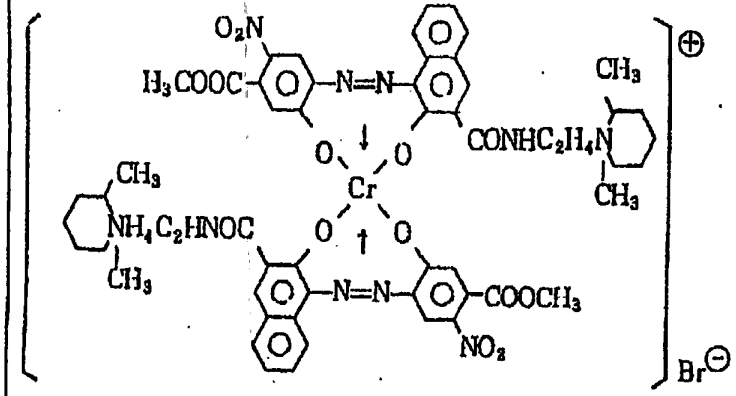
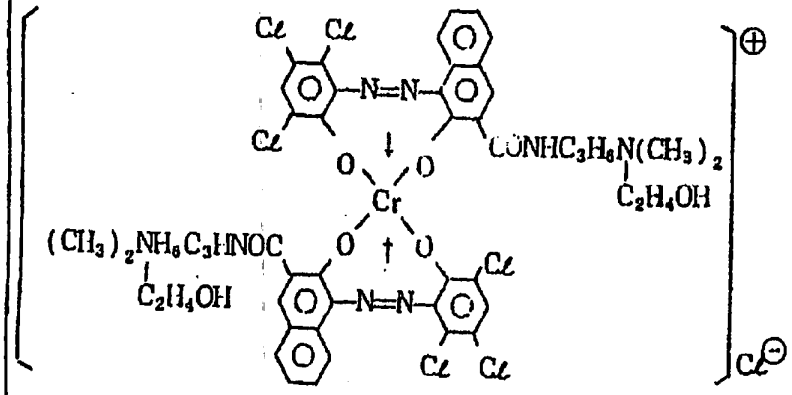
Table 4

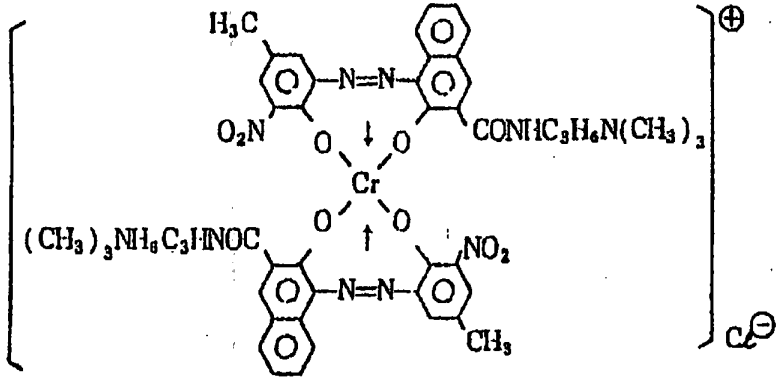
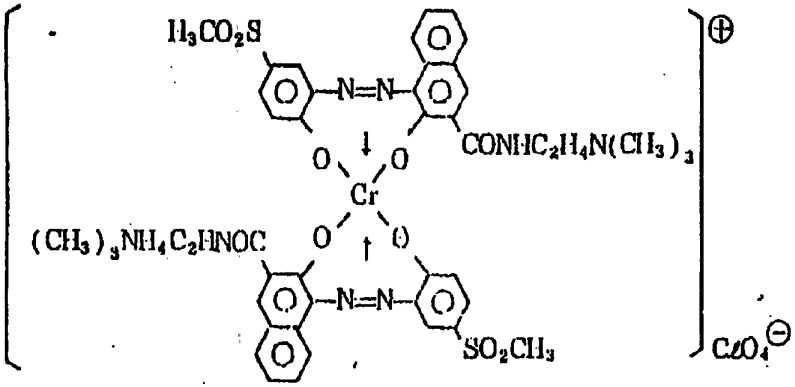
Application Examples	Composition of the developer		Electric chargeability (μc/g)
	Metal complex	Other components	
15	 0.2 part	Styrene-ethylhexyl methacrylate 40 parts Polyester resin 5 parts Silicone wax 3 parts Carbon black 2 parts Iron powder carrier 1000 parts	14.8
16	 0.5 part	Styrene-acryl copolymer 30 parts Carbon black 3 parts Glass beads carrier 1000 parts	18.9

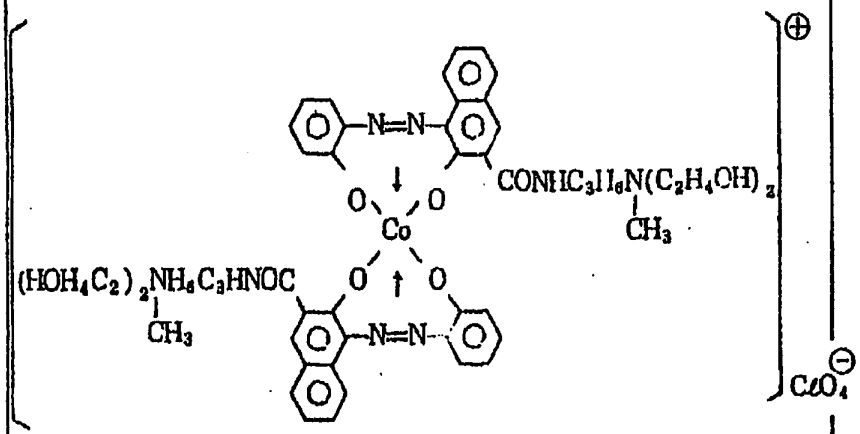
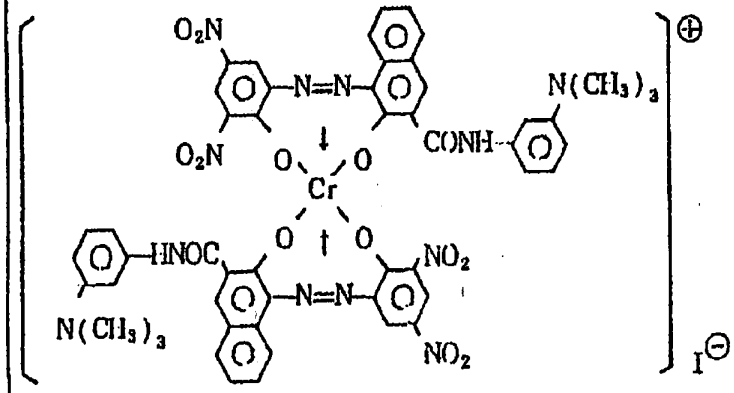
Application Examples	Composition of the developer		Electric chargeability (μc/g)
	Metal complex	Other components	
17	 1^ parts	Sytrene-methyl methacrylate copolymer 50 parts Silicone resin-coated iron powder carrier 1500 parts	16.3
18	 2 parts	Polyvinyl butyral resin 200 parts Carbon black 10 parts Iron powder carrier 2000 parts	17.4

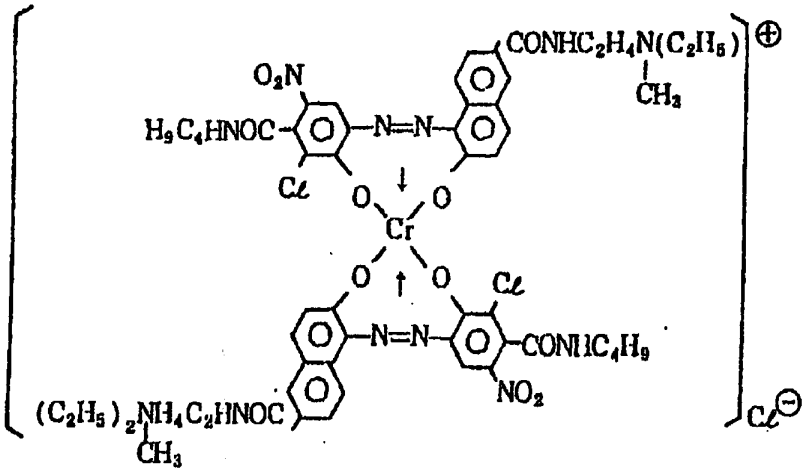
Application Examples	Composition of the developer		Electric chargeability (μc/g)
	Metal complex	Other components	
19	 0.5 part	Bisphenol type epoxy resin 50 parts Carbon black 2 parts Iron powder carrier 1000 parts	18.6
20	 0.5 part	Styrene resin 50 parts Carbon black 2 parts Iron powder carrier 1000 parts	14.0

Application Examples	Composition of the developer		Electric chargeability (μc/g)
	Metal complex	Other components	
21	 0.2 part	Styrene-butyl methacrylate copolymer 30 parts Carbon black 2 parts Iron powder carrier 800 parts	15.0
22	 0.5 part	Phenol resin 15 parts Polyester resin 8 parts Carbon black 2 parts Silicon resin-coated iron powder carrier 700 parts	21.3

Application Examples	Composition of the developer		Electric chargeability (μc/g)
	Metal complex	Other components	
23	 1 part	Polyethylene wax 50 parts Ethylene-vinyl acetate copolymer 40 parts Magnetite 30 parts	18.5
24	 0.5 part	Styrene-ethylhexyl methacrylate copolymer 20 parts Carbon black 1 part Iron powder carrier 600 parts	23.2

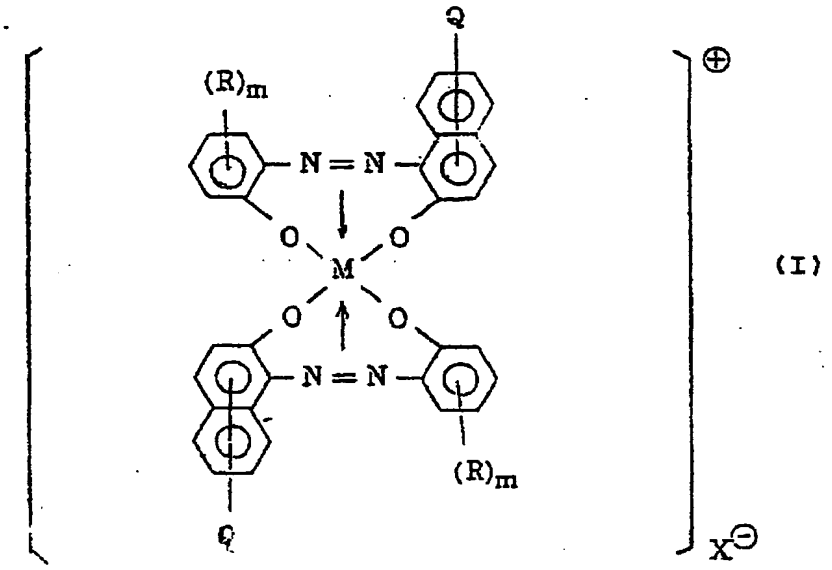
Application Examples	Composition of the developer		Electric chargeability (μc/g)
	Metal complex	Other components	
25	 0.2 part	Maleic acid resin 50 parts Carbon black 5 parts Iron powder carrier 1000 parts	16.4
26	 0.1 part	Styrene-ethyl methacrylate copolymer 30 parts Carbon black 3 parts Iron powder carrier 500 parts	18.3

Application Examples	Composition of the developer		Electric chargeability (μc/g)
	Metal complex	Other components	
27	 1 part	Styrene-butadiene copolymer 50 parts Carbon black 5 parts Iron powder carrier 1500 parts	16.7
28	 0.4 part	Polyester resin 12 parts C.I. pigment blue-15 0.2 part Silicone resin-coated iron powder carrier 400 parts	18.5

Application Examples	Composition of the developer		Electric chargeability (μc/g)
	Metal complex	Other components	
29	 2 parts	Styrene-butyl methacrylate copolymer 100 parts Carbon black 5 parts Iron powder carrier 300 parts	17.2

CLAIMS:

1. A symmetric 2 : 1 metal complex represented by the general formula:



(I)

where R is a hydrogen atom, an alkyl group having from 1 to 10 carbon atoms, an alkoxy group having from 1 to 4 carbon atoms, an alkoxycarbonyl group having from 2 to 5 carbon atoms, an acyl group having from 2 to 5 carbon atoms, an aminocarbonyl group, an alkylaminocarbonyl group having from 2 to 5 carbon atoms, an alkylsulfonyl group having from 1 to 3 carbon atoms, an aminosulfonyl group, an acylamino group having from 2 to 5 carbon atoms, a nitro group, a cyano group or a halogen atom, m is an integer of from 1 to 4, when m is 2 or more, the plurality of R may be the same or different substituents, Q is -NHCO-Y-Z or -CONH-Y-Z (where Y is an alkylene group

having from 1 to 4 carbon atoms, and Z is a quaternary ammonium group), M is a chromium atom or a cobalt atom, and $X^{\ominus}$ is an anion.

2. The metal complex according to Claim 1, wherein $X^{\ominus}$ is a halogen ion.

3. An electrophotographic toner containing the metal complex of the formula I as defined in Claim 1, as an electric charge-controlling agent or a coloring agent.

4. The electrophotographic toner according to Claim 3, which comprises from 1 to 50% by weight of the metal complex of the formula I and from 50 to 99% by weight of a resin.

5. The electrophotographic toner according to Claim 4, wherein the resin is a styrene polymer, a substituted styrene polymer, a styrene-substituted styrene copolymer, a styrene-acrylate copolymer, a styrene-methacrylate copolymer, a styrene-acrylonitrile copolymer, a polyvinyl chloride resin, a polyethylene resin, a silicone resin, a polyester resin, a polyurethane resin, a polyamide resin, an epoxy resin, a modified rosin or a phenol resin.
phenol resin.

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